Challenges in Determining the Water Quality of Storm Runoff from Caltrans Highways and Facilities

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Introduction

OBJECTIVE:

To develop suitable sampling and analytical techniques for monitoring metals and organics in storm runoff samples from Caltrans highways and facilities to establish compliance with CTR Water Quality Standards as established by EPA.

EPA RULING FOR THE STATE OF CALIFORNIA:

California Toxic Rule (CTR)

Establishes numeric criteria for priority toxic pollutants for waters in the State of California to protect human health and the environment.

Challenges in Monitoring Organic Pollutants:

- **Selection of Sites to Ensure Collection of Large Sample Volume**
- **Real-time Sampling *in-situ***
  - Rain sampler and design
  - Composite auto sampler
  - VOC-specialized equipment for volatiles
- **Development of Analytical Strategies for Over 100 Compounds**
- **Enhancement of Detection Limits**
  a. High volume storm water
  - sample (15 – 40L)
  b. Analytical methods:
  - use of selected ion monitoring for GC-MS

		Freshwater		Saltwater		Human Risk (10^{-6} risk for carcinogens) For consump. of:	
Compound	CAS No.	Crit.Cont-in. Conc.	Crit. Max. Conc.	Crit.Cont-in. Conc.	Crit. Max. Conc.	Water & Org.(ug/L)	Org. only (ug/L)
2,4-dinitrophenol	51285					70	14,000
Pentachlorophenol	87865	19	15	13	7.9	0.28	8.2
Vinyl Chloride	75014					2	525
N-nitroso-diphenylamine	86306					5.0	16
2,3,7,8-TCDD	1746016					0.00000013	0.00000014

Sites

The Highway 80 and the Maintenance yard sites were surveyed to ensure that the drainage area would supply sufficient volume for sample collection. These sites were selected as representative sites of California highways, and Caltrans maintenance yards.

HIGHWAY SITE

Figure 1. Highway 80 site before construction. Site located between Vacaville and Fairfield off of the Cherry Glen Exit.

Figure 2. Composite autosampler, rain sampler, and VOC autosampler installed at the Highway 80 site.

MAINTENANCE YARD

Figure 3. Maintenance Yard site before construction. Site located on West Texas Blvd. in Fairfield.

Figure 4. Composite autosampler, rain sampler, and VOC autosampler installed at the Maintenance Yard.

Real Time Sampling

High volume water sampling has been adopted to achieve the sensitivity required by CTR for detection of the semi-volatile compounds. Field equipment has been modified for real-time sampling to accurately determine the dissolved versus particulate contaminant levels in storm water. Filtration therefore must be performed real-time and *in-situ*.

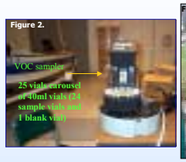


Figure 2.

Figure 3.

Real-time Sampling

Real-time sampling of storm water is achieved by 3 types of automated field equipment: volatile organic compound (VOC) autosampler for VOCs, a composite sampler for semi-volatiles (figure 1) and an automated rain sampler for airborne contaminants. Each equipment is powered by a 12 V battery that is continuously recharged by a solar panel.

Figure 1.

VOC Sampling

The VOC sampler (Isco, model 6100) (figure 2) is designed for the collection of volatile organic compounds (VOCs). The sampler is connected to the composite autosampler by an external cable, which enables the VOC sampler once the composite sampler starts pumping. The intake tubing of the VOC sampler is placed in the storm water reservoir (Figure 3). The autosampler has a Teflon bladder pump with a built-in air compressor that allows for sample integrity. The samples are collected in 40 mL amber glass vials with Teflon caps that form a gas-tight seal. The VOC sampler is programmed for gradual collection, one vial every 8 min. for a total of 5 vials in 40 min. Thus, for each storm event, 5 VOC vials are collected and transported to the laboratory on ice. VOC samples are analyzed using a Tekmar purge and trap that is connected to an Agilent gas chromatograph and mass spectrometer.

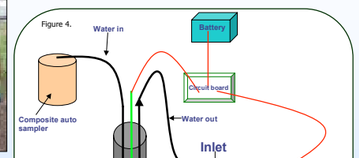


Figure 4.

Composite Sampling

The composite autosampler set-up is designed for the collection of high volume water. The sampling equipment (figure 4) consists of an Isco autosampler (model 6712), an Isco tipping-bucket rain gauge (model 674), a glass fiber filter assembly (Filterite), a 38 L holding vessel (milk can) equipped with a level sensor, PTFE diaphragm pump, serial XAD-2 glass columns, and a 25 L carboy. All components of this unit, with the exception of the 25 L carboy, are constructed of Teflon, glass or stainless steel to preclude the collection of undesirable organic contaminants.

The rain gauge is programmed to activate the autosampler when the rainfall reaches a pre-set level, for example 1.25 cm (0.5 in) of rain. Storm water collection is programmed for gradual collections, 3.5 L for every 4 min for a total of 35 L in 40 min. The outlet of the pump is connected to a filtration apparatus that empties into a 38 L stainless steel milk can. The filtered water is stored in this holding vessel because the flow rate of the automated sampler is fixed at 3.5 L/min. This high flow rate cannot be used for the extraction of organics by the XAD-2 glass columns, therefore a second pump is employed. A level sensor is attached to the holding can so that some storm water (approximately 5 L) remains behind for the collection of phenolic and nitrosamine compounds. When the water level reaches a preset level of 5 L, the level sensor activates the pump that propels storm water through 2 serial XAD-2 columns (figure 5), 10 cm length 2.5 cm i.d. The XAD resin is designed to trap hydrophobic organic compounds such as polychlorinated biphenyls, polyaromatic hydrocarbons and others. The effluent from the columns is collected into a 25 L carboy for the final measurement of volume. After each storm event collection, the XAD columns are disconnected from the pump and returned on ice to the laboratory for analysis.

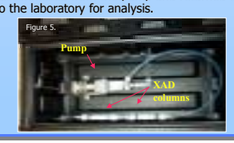


Figure 5.

Atmospheric vs Hwy Inputs

For real time *in-situ* sampling, specially constructed rain samplers have been built and deployed for assessing the contribution of atmospheric inputs versus highway inputs in storm water runoff.

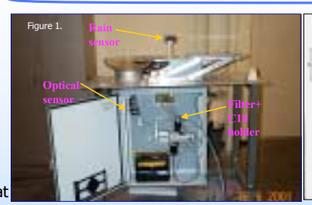


Figure 1.

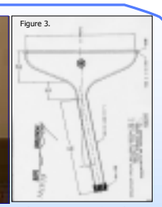


Figure 3.

Rain Sampling

We have designed and custom-built an automated rain sampler (Figure 1 and 2) that processes rain water on-site and in real-time. Components of this equipment are a rain sensor, 35 cm diameter custom-made glass funnel (Figure 3), PTFE -diaphragm pump, 47 mm stainless steel filter holder, a 47 mm glass fiber filter (GFF), and a 47 mm C_{18} extraction disk, circuit board and 1-gal carboy. Mounted on top of the sampler is the rain sensor that is triggered when rain falls on its grid. The sensor then signals the automated opening of the Teflon lined lid exposing the glass funnel. Rain falls into the funnel and collects into its 30 cm long funnel stem.

Attached to the funnel stem is an optical sensor, wired to the circuit board, that can detect the level of water in the stem column. When the optical sensor detects water, it sets off the pump which drives the collected rain water from the funnel stem through a GFF filter and C_{18} solid phase extraction disk. Filtered and extracted water empties into a 1-gal carboy. If the water in the funnel stem drops below the optical sensor beam, the pump switches off. After every rain event, the GFF circle and C_{18} extraction disk are collected and shipped on ice to the laboratory. The volume of water collected in the carboy is measured and recorded.

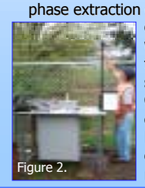


Figure 2.

CTR Toxic Pollutants

Strategy for Grouping CTR Toxic Priority Pollutants for Developing Analytical Methods

Group A:
- Benzene
- Bromoform
- Carbon Tetrachloride
- Chlorobenzene
- Chlorodibromomethane
- Dichlorobromomethane
- 1,2-Dichloroethane
- 1,1-Dichloroethylene
- 1,2-Dichloropropane
- 1,3-Dichloropropylene
- Ethylbenzene
- Methyl Bromide
- Methylene Chloride
- 1,1,2,2,-Terachloroethane
- Toluene
- 1,2-Trans-dichloroethlyene
- 1,1,1-Trichloroethane
- Vinyl chloride

Group B:
- Acrolein
- Acrylonitrile

Group C:
- 1,2-Dichlorobenzene
- 1,3-Dichlorobenzene
- 1,4-Dichlorobenzene
- 3,3'-Dichlorobenzidine

Group D:
- 2,3,7,8-TCDD

Group E:
PAHs
- Acenaphthene
- Anthracene
- Benzidine
- Benzo(a)anthracene
- Benzo(a)pyrene
- Benzo(b)fluoranthene
- Benzo(k)fluoranthene
- Fluoranthene
- Fluorene
- Pyrene
- Chrysene

E continued:
- Indeno(1,2,3-cd)pyrene
- Dibenzo(a,h)anthracene

PCBs
- 80 congeners

OC Pest.
- Alpha-BHC
- Beta-BHC
- Gamma-BHC
- Chlordane
- 4,4'-DDT
- 4,4'-DDE
- 4,4'-DDD
- Dieldrin
- Alpha-Endosulfan
- Beta-Endosulfan
- Endosulfan sulfate
- Endrin
- Aldrin
- Heptachlor
- Endrinaldehyde
- Heptachlor Epoxide

Phthalate Esters
- Bis(2-Ethylhexyl)Phthalate
- Butlbenzyl phthalate
- Diethlyphthalate
- Dimethlyphthalate
- Di-n-Butylphthalate

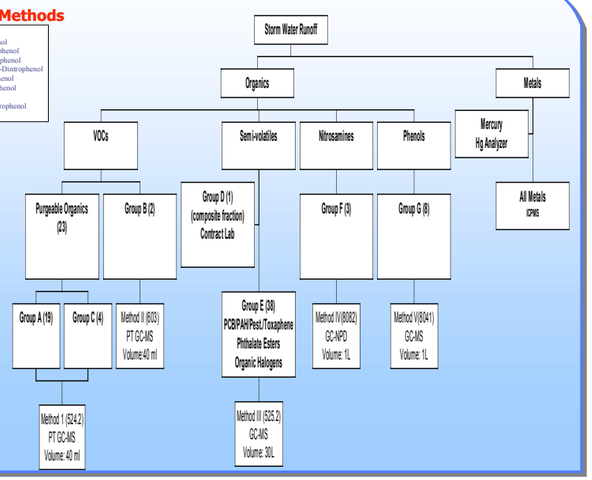
Organic Halogens
- 2-chloronaphthalene
- Hexachlorobutadiene
- Hexachlorocyclopentadiene
- Hexachloroethene

Haloethers
- Bis(2-chloroethyl) ether
- Bis(2-chloro isopropyl) ether

Other
- Toxaphene
- 2,4-Dinitrotoluene
- 1,2-Diphenylhydrazine
- Isophorone
- Nitrobenzene

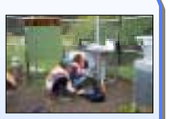
Group F:
- N-Nitrosodimethlyamine
- N-Nitrosodi-n-Propylamine
- N-Nitrosodiphenylamine

Group G:
- 2-Chlorophenol
- 2,4-Dichlorophenol
- 2,4-Dimethylphenol
- 2-Methly-4,6-Dinitrophenol
- 2,4-Dinitrophenol
- Pentachlorophenol
- Phenol
- 2,4,6-Trichlorophenol



Progress to Date

- Established field collection sites and stormwater sampling equipment for VOCs, Semi-volatiles, Nitrosamines, and Phenolics.
- VOCs were not detected in 5 storm water collections of the 2001-2002 rainy season.
- N-Nitrosamines and Phenolics analyses show exceedance of CTR criteria for N-nitrosodiphenylamine and Pentachlorphenol (Figure 1 and 2).
- Semi-volatiles in storm water and rain water are currently being analyzed.



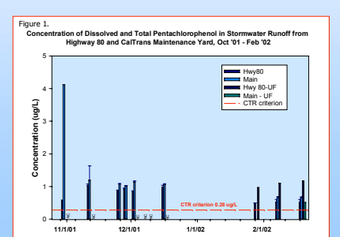


Figure 1.

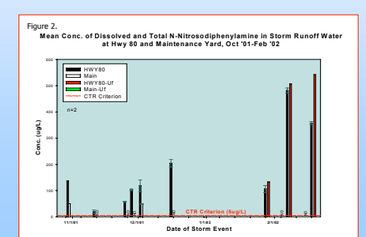


Figure 2.

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